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Diferuloylmethane anchored anatase TiO_2 nanoparticle for dye sensitized solar cell

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Dye sensitized solar cells (DSSC) have been constructed by using diferuloylmethane dye as natural photosensitizers for anatase nanostructure TiO_2 thin film coated on FTO conductive glass substrate. Structural and morphological properties of the semiconductor films have been characterized by X-ray diffractometer and scanning electron microscopy, respectively, as well as, the wavelength of the maximum absorbance of the dye anchored on TiO_2 film has been studied by using UV-Vis spectrophotometer. The XRD pattern of TiO_2 thin films made by Doctor-blading deposition technique has revealed that the grain size of TiO_2 is equal to 40 nm. The photovoltaic performance of the cells have been investigated in terms of power conversion efficiency, furthermore the effect of different spectroscopic parameters on the PV performance of constructed DSSC has been studied.

Keywords: Natural photosensitizers, Nanoparticle, Diferuloylmethane, TiO_2, Dye sensitized solar cells

1 Introduction

The conversion of solar energy to electricity appears as one of the technologies that can replace fossil fuels[1]. Solar cells, or photovoltaic (PV) cells, are electrical devices capable of directly converting sunlight into electrical power in which it is known as photovoltaic effect[2,3]. An extremely promising solar cell is dye sensitized solar cell[1,4] (DSSC), which is based on combination of dyes with metal oxides semiconductor and an electrolyte to convert sunlight into electrical power[5].

Light is absorbed by the dye or sensitizer, which is anchored to the surface of a wide band gap semiconductor[6,7]. Charge separation takes place at the interface via photoinduced electron injection from the dye into the conduction band of the nanocrystalline solids which are metal oxides, especially titanium dioxide. The anatase phase has been preferred and widely used in solar cell applications, primarily owing to its wider band gap for the maximum possible transmission[8].

The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO_2 are important parameters determining the efficiency of the cell[9]. In recent several years it has become a great attention to use DSSC based on natural dyes due to the high extinction coefficient for natural dye, and simply procedure to extract it, as well as its environmental friendliness[10-12].

Diferuloylmethane (curcumin) is natural dye as called polyphenol curcumin, C.I. 75300, and natural yellow 3, having a molecular formula $C_{21}H_{20}O_6$ and molecular weight[13-15] 368.38 $gmol^{-1}$. Diferuloylmethane is an organic compound of orange-yellow pigment obtained from the perennial herb plant of ginger family called curcuma longa commonly known as turmeric[16,17], it is native to South Asia and needs temperatures between 20 °C and 30 °C (68 °F and 86 °F) and a considerable amount of annual rainfall to thrive, used in food as a spice or as mainly ingredient in curry powders and sauces[17,18].

Diferuloylmethane can exist at least in two tautomeric forms, keto and enol, as show in Fig. 1. The keto form is preferred in solid phase and the enol form in solution[15,19]. It is hydrophobic in nature and freely soluble in dimethyl sulfoxide, acetone, methanol and ethanol[20] practically insoluble in water[18,21].

Diferuloylmethane is a promising material for use in solar cell owing to; its long intense wavelength absorption range from (420-580) nm in the visible region[22], moreover diferuloylmethane molecule has carbonyl and hydroxyl groups, which facilitate bind to the surface of TiO_2 particles, making way for electron transfer from the excited diferuloylmethane molecule to the conduction band[23,24] of TiO_2.

Several natural dyes have been utilized as sensitizer in DSSC; Kim *et al.*[6] had extracted natural curcumin dye from curcuma longa L then used as a

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sensitizer in DSSC. They were treated dye with acetic, nitric and hydrochloric acid for increasing the conversion efficiency of cell. Al-Bat'hi and her co-worker[7] constructed DSSC by using the orange-red Lawsone, red purple anthocyanin and yellow curcumin. The overall power conversion efficiency of 0.36% was obtained with the curcumin dye. Moustafa and his co-worker[9] studied the light absorption spectrum of the six dye solutions in addition the wavelength of the maximum absorbance of the curcumin dye-loaded TiO_2 film. Sorachoti[19] employed natural dyes extracted from anthocyanin, curcumin and monascus in DSSC and studied the effect of dye concentration on adsorption amount of dye on TiO_2 film.

The aim of this work is to improve the PV performance of DSSC based on diferuloylmethane (curcumin) natural dye and study the effect of some spectroscopic factors affecting on the PV performance of constructed DSSC included film thickness, dye solution concentration and the dye solvent effects.

2 Experimental

We have prepared type of dye sensitized solar cell, using natural dye which is Curcumin dye ($C_{21}H_{20}O_6$) as photosensitizers, with nanocrystalline semiconductor oxide of TiO_2 deposited and carbon coated electrode as photo and counter electrode respectively, each other deposition on conductive glass substrate FTO as photo and counter electrode, respectively, addition to these components, the electrolyte consists of iodide/tri-iodide (I^-, I_3^-) as red-ox couple in a solvent.

2.1 Materials

Diferuloylmethane dye ($C_{21}H_{20}O_6$) with M_W (368.38 g/mol) and purity more than 99% purchased from Fluka company (Switzerland), conductive glass substrate FTO (7 ohm/sq) purchased from Solaronix company (Switzerland), TiO_2 anatase nanopowder less than 50 nm grain size with purity 99.8% (China), acetone pure from Medex (United kingdom), PEG from Himedia with M_W (20.000 g/mol) (India), acetyl acetone from Riedel de Haen AG Seelz-Hnnover (Germany), dimethyl sulfoxide from BDH/Chemicals (England). All other solvent and the chemical employed for the experimental work were of laboratory grade chemicals.

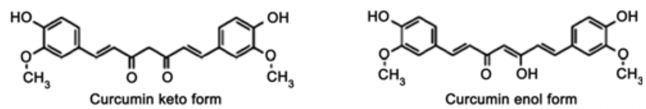

Fig. 1 — Chemical structures of diferuloylmethane (curcumin) dye[7,13]

2.2 Preparation of TiO_2 photo electrode

The photo electrode was prepared by depositing TiO_2 film on the conductive glass FTO. Prior to the film deposition, it must clearly identify the appropriate side of conductive glass substrate FTO by using a multimeter, and visually the conductive side is also the one that looks hazy. Then glass substrate was prepared by cleaning with denatured alcohol such as ethyl alcohol (purity 96%), and left to dry in air. The edges of the conductive glass were then masked with a scotch tape to give an active area of 1.5 cm^2 and to control the film thickness as well as to provide uncoated area for electrical contact. The TiO_2 paste was prepared by the incremental addition of 1.6 mL of deionized water and 0.02 mL acetyl acetone to 1 g of TiO_2 powder and 20 wt% (with respect to TiO_2 wt) of PEG (Poly ethylene glycol M_W 20,000) was added as a binder, then grinding for 30 min.

The TiO_2 paste was spread uniformly on the conducting side of substrate by Doctor-blading technique[12,25], then left it to dry at room temperature for approximately 7 min to reduce the surface irregularities. The TiO_2 layer was sintered for 30 min at 450 ºC, and then allowed to cool slowly at room temperature, thereafter dipped into the diferuloylmethane dye solution 10^{-3} M for 19 h in a dark place and by using acetone as a solvent. The substrate was rinsed with organic solvent like acetone, then left to dry and immediately used in mounted cells.

This method is repeated with changing the different spectroscopic parameters such as concentration of dye solution and the solvent for dye etc.

2.3 Preparation of counter electrode

The counter electrode is prepared by deposition a thin layer of carbon from the combustion of candle that makes a black deposition on the conducting side of FTO substrate. This thin carbon layer serves as a catalyst for the tri-iodide to iodide regeneration reaction. The edges of the substrate were then cleaned to provide uncoated area for electrical contact, thus the substrate was allowed to cool before cell assembling. The DSSC were assembled by pressed electrodes together as a sandwich configuration. One drops of electrolyte solution was injected at the edges of the substrate. By illuminating the cells with a light source, the electrical power generation is achieved and the photovoltaic capability for DSSC to produce current and voltage across each individual cell can be measured.

3 Results and Discussion

3.1 Structural properties

The structural compositions of TiO_2 films have been investigated using X-ray diffraction (XRD) pattern. Figure 2 shows the XRD pattern of TiO_2 films, the broadening in this pattern can be ascribed to increase the defects and poor crystallinity of TiO_2 particles. This result can be interpreted to the role of diferuloylmethane which increases the adsorption activity by increasing amorphous nature of TiO_2, and this result is in agreement with the earlier reported study[17]. The grain size was found to be 40 nm approximately by using Scherrer equation.

3.2 Morphological properties

Scanning electron microscopy (SEM) of the samples was carried out to estimate the surface morphology of the samples. Figure 3 shows the SEM image of TiO_2 film. It is clarified from this figure that the surface is flatting, free of cracks and the particles are spherical in shape with semi-uniform size, as well as it can be observed the decreases in porosity that indicates the dye well adsorbed on the TiO_2 particle.

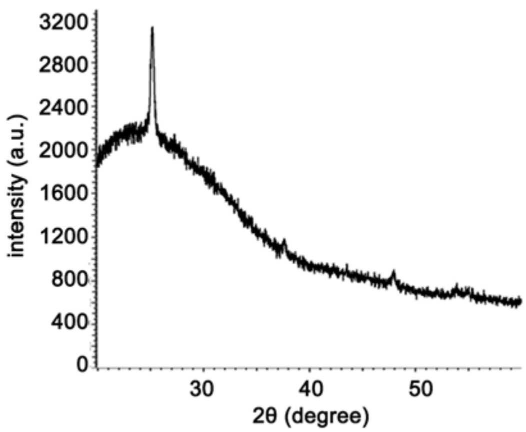

Fig. 2 — XRD pattern for TiO_2 film sensitized by diferuloylmethane dye

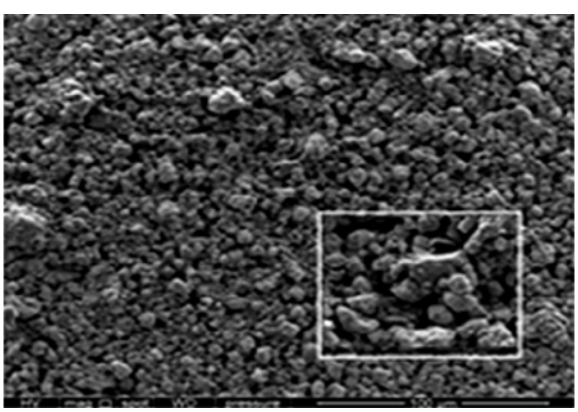

Fig. 3 — SEM image for TiO_2 film sensitized by diferuloylmethane dye

3.3 Spectroscopic properties

The UV-Visible absorption spectrum of diferuloylmethane dye solution is shown in Fig. 4. It can be seen that the peak absorption at 438 nm and the band width at full width half maximum (FWHM) is 117 nm.

3.4 Electrical properties

The electrical power generation is achieved by illumination the DSSC and determined its PV parameters across each individual cell. Figure 5 shows the directly proportional of short circuit current (I_{sc}) with the intensity of incident light for constructed DSSC. It is well known that the photocurrent of DSSC is correlated directly with the number of dye molecules. Therefore, the increase of adsorbed dye molecules led to increase the electron injection from exited dye to the conduction band of TiO_2 which consequently increases harvesting of incident light and photocurrent of cell. This results in agreement with earlier work[26,27].

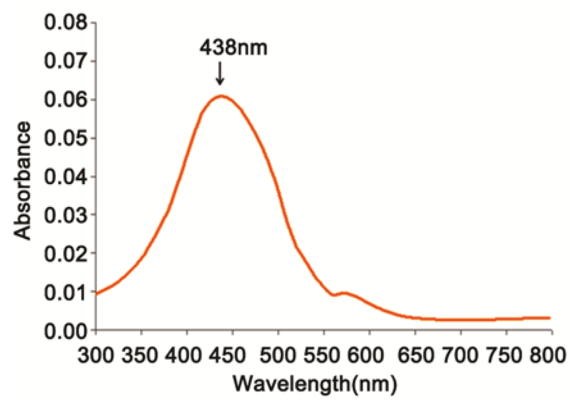

Fig. 4 — The absorption spectrum of diferuloylmethane dye

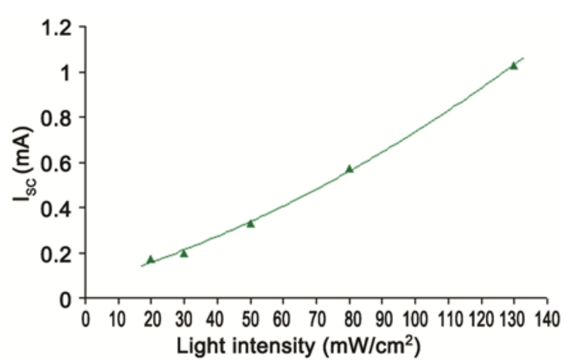

Fig. 5 — Current curves for constructed DSSC based on diferuloylmethane dye

The variation of open circuit voltage (V_{oc}) with the intensity of incident light for constructed DSSC is represented in Fig. 6. Figure 7 shows the inversely proportional of power conversion efficiency with the intensity of incident light for constructed DSSC. The promising power conversion efficiency value of 1.15% considered the highest value in comparison with previous survey[6,7,9,19,28,29] for DSSC based on diferuloylmethane dye.

Table 1 represents the PV performance of the DSSC in terms of short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (η) under different intensity of light, for active area 1.5 cm^2.

There are many spectroscopic factors that influence on the PV performance of constructed DSSC. Figure 8 shows that cell constructed with TiO_2 photo electrode of 895 nm film thickness appeared the best power conversion efficiency, because film thickness needs to be optimized for each dye owing to the different in the light absorption coefficients, and this result in consistent with[12,30].

Figure 9 illustrates the PV performance of constructed cell with different dye solution concentration.

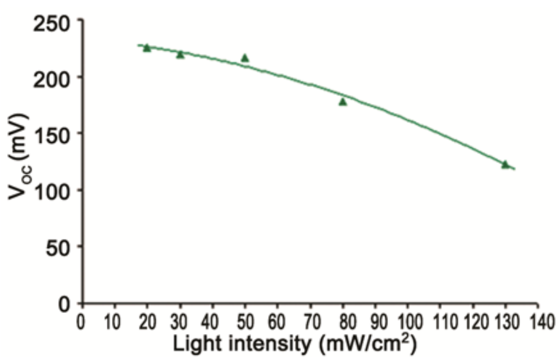

Fig. 6 — Voltage curves for constructed DSSC based on diferuloylmethane

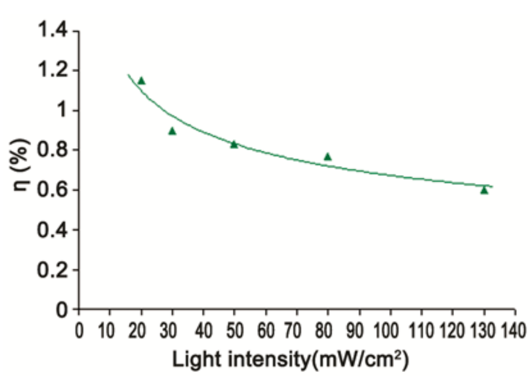

Fig. 7 — Power conversion efficiency curve for constructed DSSC based on diferuloylmethane dye

The result indicated that the highest concentration of dye solution has produced the highest power conversion efficiency due to the increase in number of dye molecules, which leads to increase the absorbance and harvesting of light.

The PV parametrs of constructed DSSC were determined with three types of dye solvents (acetone, dimethyl sulfoxide, methanol) as shown in Fig. 10. It can be observed that acetone appropriate solvent for diferuloylmethane dye to improve the power conversion efficiency of cell, due to the low acetone viscosity (0.29 cP) in comparison with dimethyl

Table 1 — Photovoltaic performance of constructed DSSC based on diferuloylmethane dye

Light intensity (mW/cm^2)	V_{oc} (mV)	I_{sc} (mA)	FF	η (%)
20	225	0.17	0.907	1.15
30	219	0.20	0.928	0.90
50	216	0.33	0.883	0.83
80	178	0.57	0.912	0.77
130	123	1.03	0.923	0.60

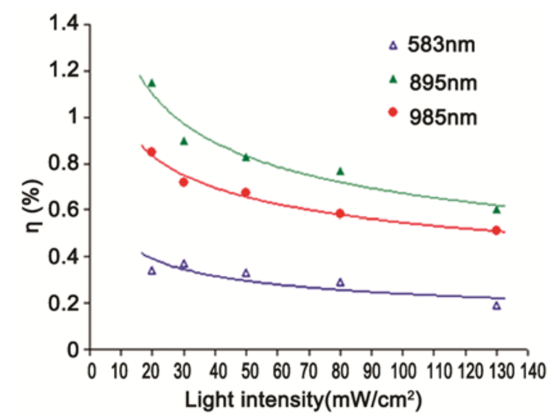

Fig. 8 — Film thickness effect on power conversion efficiency of constructed DSSC

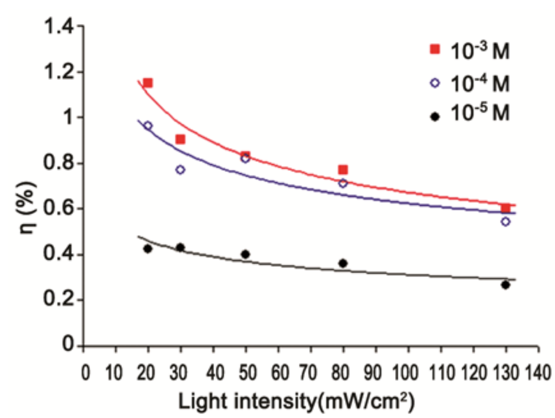

Fig. 9 — Dye solution concentration effect on power conversion efficiency of constructed DSSC

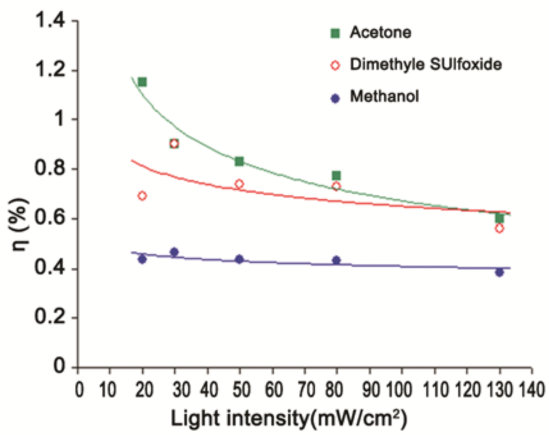

Fig. 10 — Dye solvent effect on power conversion efficiency of constructed DSS

sulfoxide (1.99 cP viscosity), in addition the polar aprotic solvent including acetone and dimethyl sulfoxide was found to be more efficient solvent for accelerated dye diffusion into TiO_2 surface in comparision with methanol polar protic solvent.

4 Conclusions

The major conclusion that can benefit from it in this work was; diferuloylmethane shows increasing defects and poor crystallinity of TiO_2 particles consequently increasing the adsorption activity by increasing amorphous nature of TiO_2. This leads to enhance the PV performance of cell in terms of power conversion efficiency, as well as film thickness need to be optimized for each dye due to the different in the light absorption coefficients. The study revealed that 895 nm film thickness of TiO_2 photo-electrode appeared the best power conversion efficiency.

The photovoltaic performance of constructed cells shows the directly proportional for photocurrent and inversely proportional for power conversion efficiency with the intensity of incident light for constructed DSSC in agreement with the theoretical concepts.

There are many spectroscopic factors that influenced the PV performance of constructed DSSC such as highest concentration of dye solution has produced the highest power conversion efficiency and the polar aprotic solvent including low viscosity such as acetone was appropriate solvent to improve the PV performance of DSSC based on diferuloylmethane dye.

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